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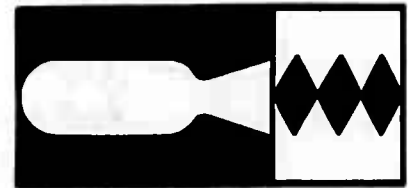
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Sixth Quarterly Report

Contract No. DA 04-495-ORD-1987

ARPA Order No. 40-61

XEROX



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**ROCKET POWER, INC.**

**Sixth Quarterly Report  
Contract No. DA 04-495-ORD-1987  
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**THERMODYNAMICS OF REACTIONS  
INVOLVING LIGHT METAL OXIDES  
AND PROPELLANT GASES**

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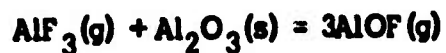
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## SUMMARY

An experiment has been performed employing a specially designed high temperature electron bombardment-resistance furnace indicating the formation of AlOF as a result of the reaction, ( $T = 2223^{\circ}\text{K}$ )



Based on the assumption that equilibrium conditions exist, a preliminary heat of formation for AlOF at  $298^{\circ}\text{K}$  of  $-128 \pm 11$  kcal/mole is obtained.

A mathematical treatment of the BOF monomer data presented in the Fourth Quarterly Report<sup>1</sup> indicates a value for the entropy at  $S_{298\text{K}}^{\text{BOF}}(\text{g})$  of  $53.1 \pm 4.2$  cal/ $^{\circ}$ /mole.

The molecule  $(\text{HBO}_2)_3$  has been studied in a transpiration experiment in which argon saturated with water is passed over heated boric oxide. The possibility that several species are present in the reaction mixture is considered, and a mathematical treatment of the data under these conditions is given.

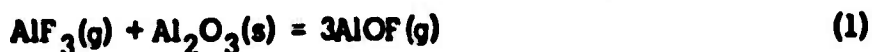
## I. INTRODUCTION

The object of this research is to obtain definitive values for the thermodynamic properties of various species which are found in the exhaust gases of high performance rocket engines; specifically the oxides and oxyhalides of the light metals such as boron and aluminum. The present report discusses work done on the molecules AlOF, BOF, HBO<sub>2</sub> and (HBO<sub>2</sub>)<sub>3</sub>.

## II. STUDY OF AlOF

### A. Introduction

The reaction chosen for the study of AlOF is the one between AlF<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>,



The reactions between Al<sub>2</sub>O<sub>3</sub> and F(g) or HF(g) to produce AlOF were excluded because of the overwhelming competition from the reactions which produce AlF<sub>3</sub> instead of AlOF. Using the data in the JANAF Tables,<sup>2</sup> it is possible to calculate the approximate experimental conditions which are necessary to make reaction (1) go to the extent that it can be studied by gravimetric techniques. Some of these calculations are given in the Fifth Quarterly Report.<sup>3</sup> The conclusion is that, even if the heat of formation of AlOF is less than that given in the JANAF Tables, the study of the reaction is not possible below about 1900°K. Experiments at 1870°K, in which AlF<sub>3</sub> vapor was passed through a sapphire tube, showed either no weight loss for the sapphire tube or an actual weight gain.

The sapphire tube was heated in a combustion furnace which has an upper temperature limit of 1870°K. To overcome this temperature limitation, a new furnace using electron bombardment or resistance heating was constructed. Since this new furnace is constructed entirely of tungsten and tantalum, it has the melting point of tantalum (3300°K) as its upper temperature limit. The reaction shown in Eq. (1) has been studied with the electron bombardment furnace, and evidence for the production of AlOF has been observed at a temperature of 2223°K and a pressure of AlF<sub>3</sub> which is estimated to be between  $6.5 \times 10^{-4}$  atm and  $8.5 \times 10^{-7}$  atm.



## B. Experimental

The properties of AlOF were studied in a transpiration experiment in which  $\text{AlF}_3$  vapor was passed through a heated  $\text{Al}_2\text{O}_3$  tube. The extent of the reaction was determined from the weight loss of the  $\text{Al}_2\text{O}_3$  tube and the flow rate of  $\text{AlF}_3$  vapor.

A schematic drawing of the apparatus is shown in Fig. 1 and photographs of the high temperature furnace and the  $\text{Al}_2\text{O}_3$  reaction vessels are shown in Figs. 2 and 3.

The high temperature furnace consists of a tube of 20 mil tantalum, one inch in diameter and three inches in length. This tube is surrounded by fine concentric radiation shields of 2 mil tantalum foil. The ends of the tube are closed by removable plugs made of three layers of 2 mil tantalum foil. Inside the tantalum tube are 12 filaments of coiled tungsten wire which run the length of the furnace. The furnace can be heated to at least  $2300^\circ\text{K}$  by direct resistance heating of these 12 filaments, or it can be heated to higher temperatures by bombarding a target with electrons which are emitted from the filaments. When it is operated as an electron bombardment furnace, the target is made several thousand volts positive with respect to the filaments. The energy that the electrons gain in falling through this potential drop is given up to heat the target.

The vacuum envelope for the furnace is a piece of commercial glass pipe (Corning Pyrex) six inches in diameter and eighteen inches in length with a 2 inch side arm. The ends of this glass pipe have grooves into which O-rings can be fitted. One end of the pipe is closed by an O-ring and an aluminum plate, the other end by an O-ring and the aluminum base plate upon which the furnace elements are supported. Electrical connections to the furnace are made through ceramic insulators in the furnace support plate.

The reaction vessel, which is also the source of  $\text{Al}_2\text{O}_3$  for the reaction, is a tube of recrystallized alumina\* with an inside diameter of  $1/8$  inch, an outside diameter of  $1/4$  inch and a length of  $3\frac{1}{2}$  inches. The reaction tube enters the furnace from the bottom. The end of the tube is about one inch from the top of the furnace. This insures that the exit end of the tube is at the maximum temperature of the furnace. If there were a decreasing temperature gradient along the tube, any AlOF which was formed would disproportionate into  $\text{AlF}_3$  and  $\text{Al}_2\text{O}_3$  at the lower temperature. The  $\text{Al}_2\text{O}_3$  would be deposited on the reaction tube, and the reaction could not be detected. The reaction tube

\*Obtained from McDanel Refractory Porcelain Company

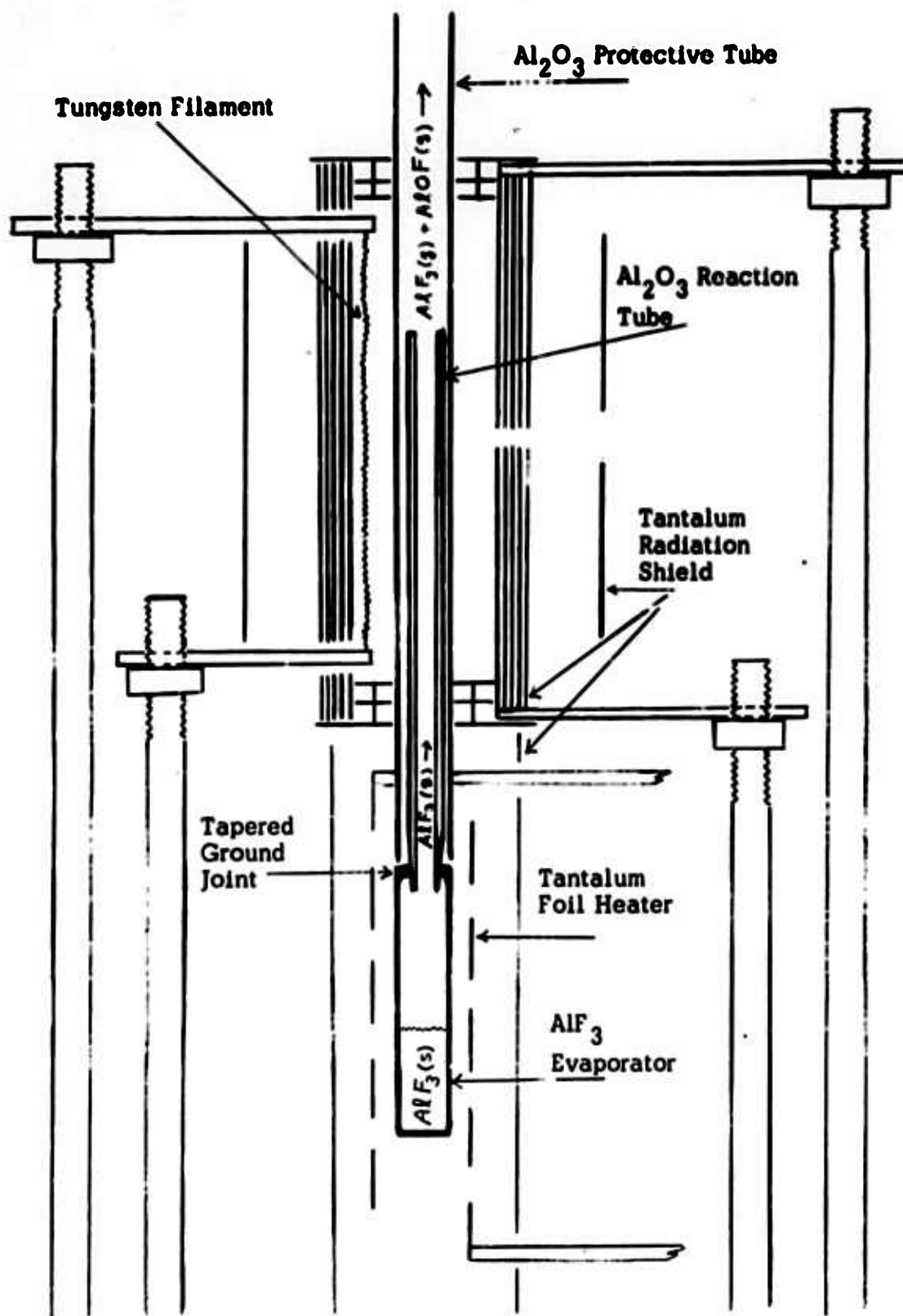


Fig. 1. Schematic Drawing of the High Temperature Furnace and the Al<sub>2</sub>O<sub>3</sub> Reaction Vessel

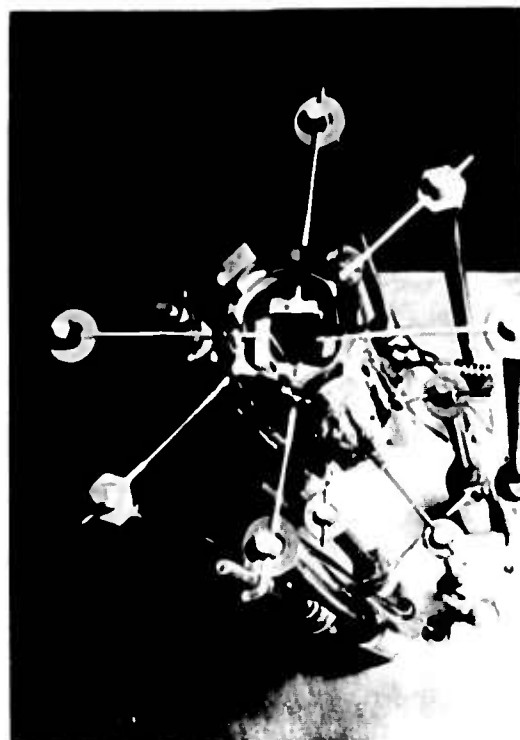
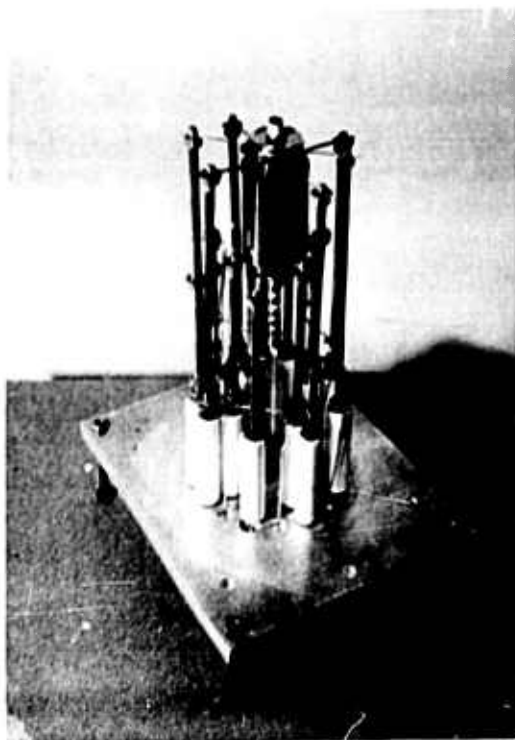
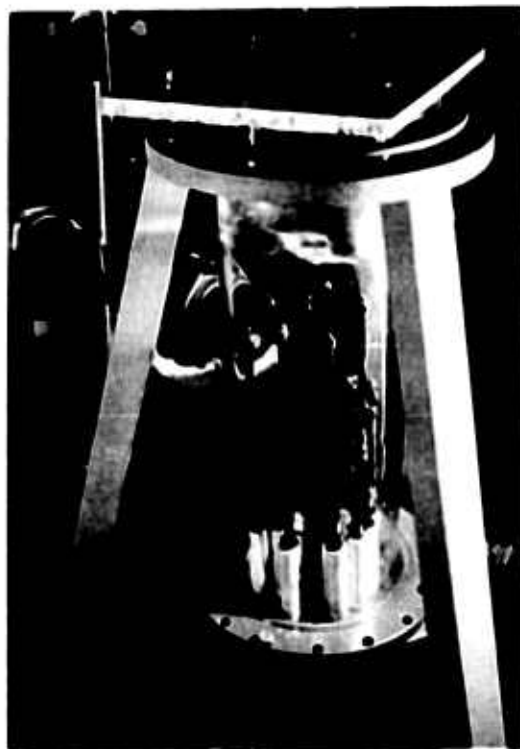


Fig. 2  
Photographs of the Electron Bombardment-Resistance  
High Temperature Vacuum Furnace

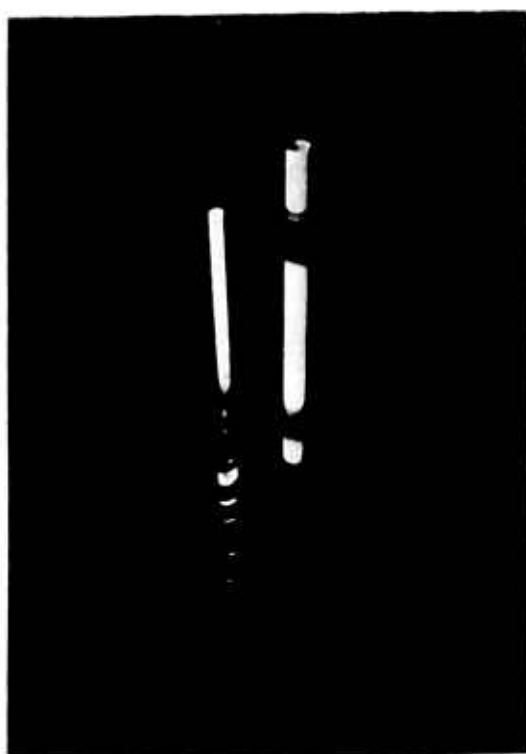


Fig. 3  
Photographs of the  $\text{Al}_2\text{O}_3$  Reaction Vessel and the  $\text{AlF}_3$   
Vapor Generator

is contained in a larger protective tube of recrystallized alumina which passes through the entire furnace. The purpose of this protective tube is to prevent condensation of tungsten and tungsten oxide on the reaction tube, and to prevent  $\text{AlF}_3$  from coming in contact with the hot tungsten filaments.

The  $\text{AlF}_3$  vapor for the reaction is generated by heating solid  $\text{AlF}_3$  in a tube made of recrystallized alumina. The tube has an inside diameter of 1/4 inch, an outside diameter of 3/8 inch, and a length of 1 5/8 inches. It is closed on one end, and it is attached to the reaction tube on the other end by means of a tapered ground joint. This tight-fitting joint insures that all of the  $\text{AlF}_3$  leaving the evaporator passes through the reaction tube, and it allows the two tubes to be separated for weighing. The tube containing the solid  $\text{AlF}_3$  is surrounded by a heater of 2 mil tantalum foil, the heater being constructed so that there is a temperature gradient increasing toward the furnace. Thus, once the  $\text{AlF}_3$  evaporates, it will not condense on the reaction tube.

During an experiment,  $\text{AlF}_3$  vapor at a given pressure, which depends on the temperature of the tantalum foil heater, passes through the reaction tube. About one-half of the reaction tube is at the maximum temperature of the furnace. At this temperature, the  $\text{AlF}_3$  vapor reacts with the inner walls of the  $\text{Al}_2\text{O}_3$  reaction tube to produce  $\text{AlOF}$ . The  $\text{AlF}_3$  and  $\text{AlOF}$  flow out of the furnace through the large  $\text{Al}_2\text{O}_3$  protective tube and condense on a metal plate. The extent of the reaction is determined by the loss in weight of the reaction tube.

### C. Discussion

An experiment at 2223°K showed a weight loss in reaction tube which indicated that a reaction had taken place to form  $\text{AlOF}$ . Since this temperature is near the melting point of  $\text{Al}_2\text{O}_3$  (2318°K), there exists the possibility that  $\text{Al}_2\text{O}_3$  is evaporating as well as reacting. Several blank runs were made in which the  $\text{Al}_2\text{O}_3$  reaction tube was heated in vacuum. The initial blank weight loss was 10 mg/hr, but it decreased to 1.3 mg/hr as the total weight loss approached one percent of the weight of the tube. The stated purity of the recrystallized alumina tube was 99 plus percent. It appears that the purity was about 99 percent, the initial high blank weight loss being due to the evaporation of impurities.

Brewer<sup>4</sup> has proposed the following mechanism for the evaporation of liquid  $\text{Al}_2\text{O}_3$



If this same mechanism holds for evaporation of the solid, the vapor pressure of  $\text{AlO(g)}$  at  $2223^\circ\text{K}$ , based on the data in the JANAF Tables, is  $1.0 \times 10^{-7}$  atm. The minimum pressure in the vacuum system during the experiment was  $8.5 \times 10^{-7}$  atm. Therefore, it appears reasonable to expect some weight loss due to the evaporation of  $\text{Al}_2\text{O}_3(\text{s})$ .

The temperature was measured with a Leeds and Northrup optical pyrometer which was calibrated against the melting point of  $\text{Al}_2\text{O}_3$ . The  $\text{Al}_2\text{O}_3$  melted at an observed temperature of  $2278^\circ\text{K}$  as compared with the published value for the melting point of  $2318^\circ\text{K}$ . The radiation coming from inside the furnace apparently approached that of a black body. A piece of the recrystallized alumina tube was used for the calibration. Since it had not been previously heated, it could have contained up to one percent impurity which would have lowered its melting point. Because of the rather close agreement between the observed and published values for the melting point of  $\text{Al}_2\text{O}_3$ , the observed temperature was taken to be the true temperature.

The furnace was evacuated with a three-stage oil vapor pump of 25 liters/sec capacity. Because of the low pumping speed and the degassing of the furnace, the best vacuum possible was between  $1 \times 10^{-3}$  mm Hg and  $6 \times 10^{-4}$  mm Hg.

The flow of  $\text{AlF}_3$  vapor in the reaction tube produced a pressure drop which, under conditions of molecular flow, is given by<sup>5</sup>

$$P_2 - P_1 = \frac{Q}{F}$$

$$F = K \times 11.428 a^2 \sqrt{\frac{T}{M}}$$

where

- $P_2 - P_1$  = pressure drop along tube
- $Q$  = flow rate of gas
- $F$  = conductance of tube
- $K$  = Clausing factor for tube
- $a$  = radius of tube
- $T$  = temperature
- $M$  = molecular weight of gas

That section of the tube which was in the furnace has an inside diameter of 0.3 cm and a length of 5 cm. These dimensions give a Clausing factor of 0.0761 and a conductance of 0.1 liter/sec. At a flow rate of  $3.58 \times 10^{-7}$  moles/sec, the pressure drop,  $P_2 - P_1$ , is  $6.5 \times 10^{-4}$  atm. Since the pressure at the exit end of the tube is  $8.5 \times 10^{-7}$  atm,  $P_2 \approx 6.5 \times 10^{-4}$  atm. Thus, the pressure of  $\text{AlF}_3$  in various parts of the reaction tube varies between the limits of  $6.5 \times 10^{-4}$  atm and  $8.5 \times 10^{-7}$  atm.

The equilibrium constant for the formation of  $\text{AlOF}$  is given by the expressions

$$K = \frac{(3a)^2 P^2}{(1-a)(1+a)^2}$$

where

$a$  = extent of the reaction

$P$  = total pressure

The experimental data are summarized in Table I. At  $2223^\circ\text{K}$ , a value for  $a$  of 0.141 was measured. If the pressure is taken as the maximum pressure in the reaction tube,  $6.5 \times 10^{-4}$  atm, the equilibrium constant for the formation of  $\text{AlOF}$  is  $7.48 \times 10^{-9}$ ; and if the pressure is taken as the minimum pressure in the vacuum system,  $8.5 \times 10^{-7}$  atm, the equilibrium constant is  $1.27 \times 10^{-14}$ . The corresponding values for the free energy of the reaction calculated from the relationship

$$\Delta F = -RT \ln K$$

are 82.7 and 141 kcal/mole. These values combined with the data in the JANAF Tables for  $\text{Al}_2\text{O}_3(\text{s})$  and  $\text{AlF}_3(\text{g})$  give a value for  $\Delta F_{f2223\text{K}}^{\text{AlOF}(\text{g})}$  of  $-122 \pm 10$  kcal/mole. Use of the  $(F-H_{298})/T$  data in the JANAF Tables for  $\text{Al}_2\text{O}_3(\text{s})$ ,  $\text{AlF}_3(\text{g})$  and  $\text{AlOF}(\text{g})$  gives a value for  $\Delta H_{f298\text{K}}^{\text{AlOF}(\text{g})}$  of  $-128 \pm 11$  kcal/mole as compared with the calculated value of  $-121 \pm 20$  kcal/mole. This preliminary value is based on the assumption that equilibrium conditions exist, but no experimental verification of this assumption has been made.

TABLE I  
EXPERIMENTAL DATA FOR THE REACTION  
 $\text{Al}_2\text{O}_3 + \text{AlF}_3 = 3\text{AlOF}$

T (°K)	Total Pressure (atm)	Blank Weight Loss of $\text{Al}_2\text{O}_3$ (mg/hr)	Weight of $\text{Al}_2\text{O}_3$ Reacting (mg/hr)	Weight of $\text{AlF}_3$ Transpired (mg/hr)	$\epsilon$	K	$\Delta F$ Reaction (kcal/mole)
2223	$6.5 \times 10^{-4}$ $8.5 \times 10^{-7}$	1.3	18.3	108.2	0.141	$3.64 \times 10^{-9}$ $6.2 \times 10^{-15}$	88.5 144



#### **D. Future Work**

The large uncertainty in the heat of formation of AlOF is due primarily to the uncertainty in pressure. An effusion cell is more suitable for the study of this reaction since the pressure of both  $\text{AlF}_3$  and AlOF can be accurately calculated from the flow rates of these materials and the dimensions of the orifice. Varying the orifice size also gives information about the attainment of equilibrium.

During the next report period an aluminum oxide effusion cell will be used in the study of AlOF. A vacuum system with a pumping speed of 750 liters/sec is under construction and will be used to produce the necessary low pressures for the effusion cell experiments.

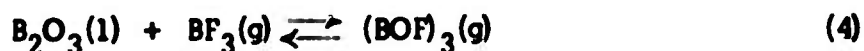
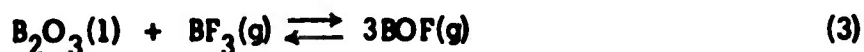
### III. THERMODYNAMICS OF MONOMER BOF

#### A. Introduction

In the Fourth Quarterly Report<sup>1</sup> a value of  $-142 \pm 3$  kcal/mole for the heat of formation of the monomer BOF at 298°K was reported. This value was determined by means of a third law analysis of data obtained by means of a new experimental technique known as Molecular Flow Reaction Studies. The third law method for analyzing data requires a use of entropies obtained from another source. As a consequence, the entropy change for the reaction under study is not determined. In the present report the results of a least squares analysis of the data presented in the Fourth Quarterly Report<sup>1</sup> for both the entropy and the heat of formation of monomer BOF are given. In the analysis which follows account is also taken of any trimer,  $(\text{BOF})_3$ , which may be present.

#### B. Theory

In this analysis it will be assumed that the following two reactions are occurring at every temperature:



The following expressions will be used in the derivation of the equilibrium constant for reaction (3):

$P_{\text{BOF}}$  = the partial pressure of BOF

$P_{(\text{BOF})_3}$  = the partial pressure of  $(\text{BOF})_3$

$P_{\text{BF}_3}$  = the partial pressure of  $\text{BF}_3$

$P$  = the total pressure

$\sqrt{\text{BOF}}$  = moles of BOF that leave the reaction zone in one hour

$\sqrt{(\text{BOF})_3}$  = moles of  $(\text{BOF})_3$  that leave the reaction zone in one hour

$\sqrt{'}_{\text{BOF}}$  = moles of BOF formed or colliding with the reaction surface per hour

$$\sqrt{'}_{\text{BOF}} = \frac{P_{\text{BOF}}(3600)A}{(2\pi RTM_{\text{BOF}})^{1/2}} \quad (5)$$

$\sqrt{'}_{(\text{BOF})_3}$  = moles of  $(\text{BOF})_3$  formed or colliding with the reaction surface per hour

$$\sqrt{'}_{(\text{BOF})_3} = \frac{P_{(\text{BOF})_3}(3600)A}{(2\pi RTM_{(\text{BOF})_3})^{1/2}} \quad (6)$$

$\sqrt{'}_{\text{BF}_3}$  = moles of  $\text{BF}_3$  that strike the reaction surface per hour

$$\sqrt{'}_{\text{BF}_3} = \frac{P_{\text{BF}_3}(3600)A}{(2\pi RTM_{\text{BF}_3})^{1/2}} \quad (7)$$

A = Area of reaction surface

$\sqrt{'}_{\text{B}_2\text{O}_3}$  = Moles of  $\text{B}_2\text{O}_3$  that react and leave the reaction surface per hour

$M_{\text{BOF}}$  = Molecular weight of BOF

$M_{(\text{BOF})_3}$  = Molecular weight of  $(\text{BOF})_3$

$M_{\text{BF}_3}$  = Molecular weight of  $\text{BF}_3$

$\sqrt{'}_{\text{BOF}}/\sqrt{'}_{\text{BOF}}$  = Ratio of molecules leaving to those formed and entering the reaction zone during one hour

$\sqrt{'}_{(\text{BOF})_3}/\sqrt{'}_{(\text{BOF})_3}$  = Ratio of molecules leaving to those formed and entering the reaction zone during one hour

$\sqrt{P_{BF_3}} / \sqrt{P'_{BF_3}} =$  Ratio of molecules leaving to those striking the reaction surface in one hour

The ratio of escape is independent of the type of molecule (6); therefore, we obtain

$$\sqrt{P_{BOF}} / \sqrt{P'_{BOF}} = \sqrt{P_{BF_3}} / \sqrt{P'_{BF_3}} \quad (8)$$

and

$$\sqrt{P_{(BOF)_3}} / \sqrt{P'_{(BOF)_3}} = \sqrt{P_{BF_3}} / \sqrt{P'_{BF_3}} \quad (9)$$

Upon substituting for  $\sqrt{P_{BOF}}$ ,  $\sqrt{P_{(BOF)_3}}$ , and  $\sqrt{P'_{BF_3}}$ , we obtain

$$P_{BOF} = \left( \frac{M_{BOF}}{M_{BF_3}} \right)^{1/2} \left( \frac{\sqrt{P_{BOF}}}{\sqrt{P_{BF_3}}} \right) P_{BF_3} \quad (10)$$

and

$$P_{(BOF)_3} = \left( \frac{M_{(BOF)_3}}{M_{BF_3}} \right)^{1/2} \left( \frac{\sqrt{P_{(BOF)_3}}}{\sqrt{P_{BF_3}}} \right) P_{BF_3} \quad (11)$$

The total pressure in dynes per sq. cm. over the reaction zone is

$$P = P_{BOF} + P_{(BOF)_3} + P_{BF_3} \quad (12)$$

On substituting for  $P_{BOF}$ ,  $P_{(BOF)_3}$ , and  $P_{BF_3}$ , we obtain

$$P = P_{BF_3} \left[ 1 + \left( \frac{M_{BOF}}{M_{BF_3}} \right)^{1/2} \left( \frac{\sqrt{P_{BOF}}}{\sqrt{P_{BF_3}}} \right) + \left( \frac{M_{(BOF)_3}}{M_{BF_3}} \right)^{1/2} \left( \frac{\sqrt{P_{(BOF)_3}}}{\sqrt{P_{BF_3}}} \right) \right] \quad (13)$$

At all times the following material balance is valid:

$$\sqrt{B_2O_3} = 1/3 \sqrt{BOF} + \sqrt{(BOF)_3} \quad (14)$$

Similarly we have

$$M_{(BOF)_3} = 3M_{BOF} \quad (15)$$

On solving equation (14) for  $\sqrt{(BOF)_3}$  and substituting the resulting expression into equation (13), we obtain

$$P_{BF_3} = \frac{P \sqrt{BF_3}}{\sqrt{BF_3} + \left( \frac{M_{BOF}}{M_{BF_3}} \right)^{1/2} \left[ \sqrt{3} B_2O_3 + 1 - \frac{1}{\sqrt{3}} BOF \right]} \quad (16)$$

Upon substituting equation (16) into equation (11) for  $P_{BF_3}$ , we obtain

$$P_{(BOF)_3} = \frac{P \left( \frac{M_{BOF}}{M_{BF_3}} \right)^{1/2} \left[ \sqrt{3} B_2O_3 - \frac{1}{\sqrt{3}} BOF \right]}{\sqrt{BF_3} + \left( \frac{M_{BOF}}{M_{BF_3}} \right)^{1/2} \left[ \sqrt{3} B_2O_3 + 1 - \frac{1}{\sqrt{3}} BOF \right]} \quad (17)$$

The equilibrium expression for reaction (4) is as follows:

$$K_2 = \frac{P_{(BOF)_3}}{P_{BF_3}} \quad (18)$$

On substituting equations (16) and (17) into equation (18), we obtain

$$K_2 = \frac{\left( \frac{M_{BOF}}{M_{BF_3}} \right)^{1/2} \left[ \sqrt{3} B_2O_3 - \frac{1}{\sqrt{3}} BOF \right]}{\sqrt{BF_3}} \quad (19)$$

which rearranges to

$$\sqrt{P_{\text{BOF}}} = \sqrt{3 P_{\text{B}_2\text{O}_3}} - K_2 \left( \frac{3 M_{\text{BF}_3}}{M_{\text{BOF}}} \right)^{1/2} \sqrt{P_{\text{BF}_3}} \quad (20)$$

The equilibrium expression for reaction (3) is as follows:

$$K_1 = \frac{P_{\text{BOF}}^3}{P_{\text{BF}_3}} \quad (21)$$

Upon substituting equation (10) into equation (21) for  $P_{\text{BOF}}$ , we obtain

$$K_1 = \left( \frac{M_{\text{BOF}}}{M_{\text{BF}_3}} \right)^{3/2} \left( \frac{\sqrt{P_{\text{BOF}}}}{\sqrt{P_{\text{BF}_3}}} \right)^3 P_{\text{BF}_3}^2 \quad (22)$$

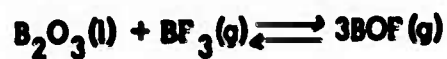
and on substituting equations (16) and (20) into equation (22), we obtain

$$K_1 = \frac{\left( \frac{M_{\text{BOF}}}{M_{\text{BF}_3}} \right)^{3/2} \left[ \sqrt{3 P_{\text{B}_2\text{O}_3}} - K_2 \left( \frac{3 M_{\text{BF}_3}}{M_{\text{BOF}}} \right)^{1/2} \sqrt{P_{\text{BF}_3}} \right]^3 P_{\text{BF}_3}^2}{\left\{ 1 + \left( \frac{M_{\text{BOF}}}{M_{\text{BF}_3}} \right)^{1/2} \left[ \sqrt{3 P_{\text{B}_2\text{O}_3}} + \frac{1-\sqrt{3}}{3} K_2 \left( \frac{3 M_{\text{BF}_3}}{M_{\text{BOF}}} \right)^{1/2} \sqrt{P_{\text{BF}_3}} \right] \right\}^2} \quad (23)$$

### C. Analyses of Experimental Data

Equation (23) may be used to determine the values of both of the equilibrium constants from a properly selected set of equilibrium data, or it may be used to evaluate one of the constants if the value of the second constant is known. In the present instance the data have not been taken in a manner which would allow the determination of both of the constants. As a consequence, in order to obtain values for  $K_1$ , it becomes necessary to obtain the values of  $K_2$  from another source. We have taken our values of  $K_2$  from Ref. 2. The resulting values of  $K_1$  are listed in Table II.

**TABLE II**  
**THERMODYNAMIC PROPERTIES FOR THE EQUILIBRIUM**



Run No.	Temp. (°K)	$K_p$	$\Delta F$ kcal	$\Gamma_{\text{BOF}}/\Gamma_{(\text{BOF})_3}$
103	1000	-	-	0
104	1000	-	-	0
105	1100	$2.48 \times 10^{-11}$	53.4	16.4
106	1100	$8.92 \times 10^{-12}$	55.6	10.7
107	1200	$1.51 \times 10^{-10}$	53.9	66.2
108	1200	$3.57 \times 10^{-10}$	51.9	66.2
109	1200	$9.62 \times 10^{-10}$	49.5	154.8
110	1007	-	-	0
111	1148	$5.67 \times 10^{-11}$	53.9	18.4
112	1054	$4.83 \times 10^{-15}$	69.0	0.6
113	1150	$3.78 \times 10^{-11}$	54.9	18.4
114	1098	$5.54 \times 10^{-13}$	61.6	3.0
115	1203	$1.65 \times 10^{-10}$	53.8	31.1
116	1075	$4.99 \times 10^{-14}$	65.4	1.3
117	1174	$3.39 \times 10^{-11}$	56.2	15.2
118	1151	$9.11 \times 10^{-12}$	58.1	8.8
119	1253	$3.72 \times 10^{-10}$	54.1	44.6
120	1252	$7.61 \times 10^{-10}$	52.2	78.9
121	999	-	-	0

According to theory, the values of  $K_1$  are related to the absolute temperature in the following manner:

$$\log K_1 = \left( \frac{\Delta S_R}{2.303R} \right) - \left( \frac{\Delta H_R}{2.303R} \right) \left( \frac{1}{T} \right) \quad (24)$$

Where  $\Delta S_R$  is the entropy change and  $\Delta H_R$  is the enthalpy change for the reaction under study. The values of  $\Delta S_R$  and  $\Delta H_R$  were evaluated by means of a least squares treatment of the experimental data. The results are tabulated in Table III. In this analysis it was necessary to neglect that data taken at temperatures below 1050°K as calculations indicated that the product was nearly 100% trimer at these temperatures. This resulted in meaningless values for  $K_1$  under these conditions. The values listed in Table III apply to an average temperature of 1160°K.\*

The mathematical analyses finally yields values at 298°K of  $-143.5 \pm 6$  kcal/mole for  $H_f$  and  $53.1 \pm 4$  cal/o/mole for  $S$  of the molecule BOF(g). Table IV compares these values with the theoretical and those previously reported.<sup>6</sup>

Agreement is excellent between the calculated and observed values.

#### D. Reactivity of SiO<sub>2</sub> and BF<sub>3</sub>

Some question as to the relative reactions between BF<sub>3</sub> with quartz and boric oxide have been raised by the statements of Fisher et al.<sup>7</sup> and Hildenbrand.<sup>8</sup>

The following experiments performed in this laboratory indicate that B<sub>2</sub>O<sub>3</sub> is much more reactive than quartz under the conditions in which the experiments were performed for the trimer and monomer of BOF.

1. Two pounds of BF<sub>3</sub> were passed through the quartz reaction beads with negligible amounts of reactivity. In one experiment 1 1/2 grams of B<sub>2</sub>O<sub>3</sub> were placed in a quartz boat at 400°C and BF<sub>3</sub> at a pressure of one atmosphere was passed over the boat for a period of two hours. The entire 1 1/2 grams of B<sub>2</sub>O<sub>3</sub> was consumed while the weight of the boat remained con-

\*The value obtained for  $\Delta S$  of the reaction at 1160°K is 71.3 e.u. Employing the JANAF Data<sup>2</sup> a value of  $S$  at 1160°K for BOF(g) of  $68.95 \pm 5$  cal/o/mole is obtained. This compares with the value of 70.7 cal/o/mole which is listed in the JANAF Tables<sup>2</sup>.



**TABLE III**  
**RESULTS OF A LEAST SQUARES TREATMENT OF THE DATA**

$\Delta S_r$	71.3 eu
$\sigma_{\Delta S_r}^*$	16.1 eu
$\Delta H_r$	134.8 kcal
$\sigma_{\Delta H_r}^*$	18.6 kcal

\*Standard Deviations

**TABLE IV**  
**THERMODYNAMIC PROPERTIES OF MONOMER BOF AT 298°K**

	Theoretical <sup>*</sup> kcal/°/mole	Experimental <sup>**</sup> kcal/mole	Experimental <sup>***</sup> kcal/mole
$H_{f298}^{\circ}K$	-142.9	$-143.5 \pm 6.2$	$-142 \pm 3$
$S_{298}^{\circ}K$	54.2 cal/°/mole	$53.1 \pm 4.2$ cal/o/mole	

<sup>\*</sup> Reported in JANAF Tables<sup>2</sup>

<sup>\*\*</sup> Least Squares Analyses of Experimental Data<sup>1</sup>

<sup>\*\*\*</sup> Third Law Calculation of Experimental Data<sup>1</sup>

stant to  $\pm 1$  milligram.

2. In another experiment a spillage of approximately one gram of  $B_2O_3$  was cleaned out from the quartz apparatus by passing  $BF_3$  over the hot liquid with no apparent reaction taking place with the quartz.

The following free energy calculations also support the non-reactivity between quartz and  $BF_3$ . Employing the JANAF Thermochemical Data<sup>2</sup> for the following reactions



A free energy of  $\Delta F = +29.58$  kcal and  $+36.48$  kcal is obtained for reaction (25) while a free energy of  $\Delta F = +5.32$  kcal and  $+6.52$  kcal is obtained for reaction (26) at temperatures of 1000 and 1300°K, respectively.

#### IV. THERMODYNAMICS OF THE TRIMER $(\text{HBO}_2)_3$

##### A. Introduction

Recently Meschi, Chupka, and Borkowitz<sup>9</sup> made a study of the reaction



in the temperature range between 1000 to 1500°K by means of mass spectroscopy. Their experiments were carried out at a total pressure of about 0.1 mm of Hg. At this pressure they found that the species  $(\text{HBO}_2)_3$  and  $\text{H}_3\text{BO}_3$  were also present and each to the extent of about 1% of that of the monomer  $\text{HBO}_2$ . These species are formed by the following reactions:



and



According to the theory, an increase in the total pressure should increase the concentrations of  $\text{H}_3\text{BO}_3$  and  $(\text{HBO}_2)_3$ . Accordingly, in the present work we have passed argon at one atmosphere and saturated with water vapor over the  $\text{B}_2\text{O}_3$  in the reaction vessel.

##### B. Mathematical Analysis

In the mathematical analysis of the conditions which hold at equilibrium, it will be assumed that reactions (27), (28) and (29) all occur at every temperature being considered. In the derivations which follow, the following expressions will be used:

$P$  = the total pressure in the gas phase over the reaction zone.  
 $P = 1$  (30)

$V$  = the volume of the transpired gas at the reaction temperature.

$\Gamma_{\text{H}_2\text{O}}$  = moles of  $\text{H}_2\text{O}$  which leave the reaction zone.

$\Gamma_A$  = moles of argon which leave the reaction zone.

$\Gamma_{\text{HBO}_2}$  = moles of  $\text{HBO}_2$  which leave the reaction zone.

$\Gamma_{H_3BO_3}$  = moles of  $H_3BO_3$  which leave the reaction zone.  
 $\Gamma_{(HBO_2)_3}$  = moles of  $(HBO_2)_3$  which leave the reaction zone.  
 $\Gamma_{B_2O_3}$  = moles of  $B_2O_3$  which react and leave the reaction zone

$$\Gamma_{B_2O_3} = 1/2 \Gamma_{HBO_2} + 1/2 \Gamma_{H_3BO_3} + 3/2 \Gamma_{(HBO_2)_3} \quad (31)$$

$P_{H_2O}$  = partial pressure of  $H_2O$

$$P_{H_2O} = \Gamma_{H_2O} RT/V \quad (32)$$

$P_A$  = partial pressure of argon

$$P_A = \Gamma_A RT/V \quad (33)$$

$P_{HBO_2}$  = partial pressure of  $HBO_2$

$$P_{HBO_2} = \Gamma_{HBO_2} RT/V \quad (34)$$

$P_{H_3BO_3}$  = partial pressure of  $H_3BO_3$

$$P_{H_3BO_3} = \Gamma_{H_3BO_3} RT/V \quad (35)$$

$P_{(HBO_2)_3}$  = partial pressure of  $(HBO_2)_3$

$$P_{(HBO_2)_3} = \Gamma_{(HBO_2)_3} RT/V \quad (36)$$

$K_1$  = equilibrium constant for reaction (27)

$$K_1 = P_{HBO_2} / P_{H_2O}^{1/2} \quad (37)$$

$K_2$  = equilibrium constant for reaction (28)

$$K_2 = P_{H_3BO_3} / P_{H_2O}^{3/2} \quad (38)$$

$K_3$  = equilibrium constant for reaction (29)

$$K_3 = P_{(HBO_2)_3} / P_{H_2O}^{3/2} \quad (39)$$

The total pressure in the gas phase in equilibrium over the condensed phase is equal to the sum of the partial pressures.

$$P = P_{H_2O} + P_{HBO_2} + P_{H_3BO_3} + P_{(HBO_2)_3} + P_A = 1 \quad (40)$$

On dividing equations (33), (34), (35) and (36) by equation (32), we obtain the following:

$$P_A = \left( \frac{\Gamma_A}{\Gamma_{H_2O}} \right) P_{H_2O} \quad (41)$$

$$P_{HBO_2} = \left( \frac{\Gamma_{HBO_2}}{\Gamma_{H_2O}} \right) P_{H_2O} \quad (42)$$

$$P_{H_3BO_3} = \left( \frac{\Gamma_{H_3BO_3}}{\Gamma_{H_2O}} \right) P_{H_2O} \quad (43)$$

$$P_{(HBO_2)_3} = \left( \frac{\Gamma_{(HBO_2)_3}}{\Gamma_{H_2O}} \right) P_{H_2O} \quad (44)$$

Upon substituting equations (41), (42), (43) and (44) into equation (40) we obtain

$$P = P_{H_2O} \left[ 1 + \frac{\Gamma_A + \Gamma_{HBO_2} + \Gamma_{H_3BO_3} + \Gamma_{(HBO_2)_3}}{\Gamma_{H_2O}} \right] = 1 \quad (45)$$

The material balance given by equation (31) rearranges to give

$$\Gamma_{(HBO_2)_3} = \frac{2\Gamma_{B_2O_3} - \Gamma_{H_3BO_3}}{3} \quad (46)$$

On substituting equation (46) for  $\Gamma_{(\text{HBO}_2)_3}$  into equation (45), we obtain

$$P = P_{\text{H}_2\text{O}} \left[ 1 + \frac{3\Gamma_A + 2\Gamma_{\text{B}_2\text{O}_3} + 2\Gamma_{\text{HBO}_2} + 2\Gamma_{\text{H}_3\text{BO}_3}}{3\Gamma_{\text{H}_2\text{O}}} \right] = 1 \quad (47)$$

Upon substituting equations (37) and (38) for  $P_{\text{HBO}_2}$  and  $P_{\text{H}_3\text{BO}_3}$  into equations (42) and (43) respectively, we obtain the following:

$$\Gamma_{\text{HBO}_2} = \frac{K_1 \Gamma_{\text{H}_2\text{O}}}{P_{\text{H}_2\text{O}}^{1/2}} \quad (48)$$

$$\Gamma_{\text{H}_3\text{BO}_3} = K_2 P_{\text{H}_2\text{O}}^{1/2} \Gamma_{\text{H}_2\text{O}} \quad (49)$$

On substituting equations (48) and (49) into equation (47), we obtain

$$\left( \frac{2K_2}{3} \right) P_{\text{H}_2\text{O}}^{3/2} \left( 1 + \frac{3\Gamma_A + 2\Gamma_{\text{B}_2\text{O}_3}}{3\Gamma_{\text{H}_2\text{O}}} \right) P_{\text{H}_2\text{O}} + \left( \frac{2K_1}{3} \right) P_{\text{H}_2\text{O}}^{1/2} - P = 0 \quad (50)$$

Once  $K_2$ ,  $K_3$ ,  $\Gamma_A$ ,  $\Gamma_{\text{B}_2\text{O}_3}$  and  $\Gamma_{\text{H}_2\text{O}}$  are known for a particular run, it should be possible to solve equation (50) for  $P_{\text{H}_2\text{O}}$ . The solution of the equation is easily accomplished by a method of iteration.

Upon substituting equation (39) for  $P_{(\text{HBO}_2)_3}$  into equation (44), we obtain

$$\Gamma_{(\text{HBO}_2)_3} = K_3 P_{\text{H}_2\text{O}}^{1/2} \Gamma_{\text{H}_2\text{O}} \quad (51)$$

On substituting equations (48), (49), and (51) into equation (31) and rearranging terms, we obtain

$$K_3 = \frac{2 \left( \frac{\Gamma_{\text{B}_2\text{O}_3}}{\Gamma_{\text{H}_2\text{O}}} \right) - \left( \frac{K_1}{\sqrt{P_{\text{H}_2\text{O}}}} \right) - K_2 \sqrt{P_{\text{H}_2\text{O}}}}{3 \sqrt{P_{\text{H}_2\text{O}}}} \quad (52)$$

To evaluate  $K_3$  the value of  $P_{H_2O}$  obtained from equation (50) is substituted along with the other necessary quantities into equation (52). The evaluation of  $K_3$  requires a prior knowledge of the values of  $K_1$  and  $K_2$ . The values of  $K_1$  were taken from Ref. 9, and the values of  $K_2$  were obtained from Ref. 2.

### C. Experimental

Figure 4 is a diagram of the apparatus used. Argon at a pressure of one atmosphere was passed through a drying tower filled with anhydrous  $CaCl_2$ . The dry argon was saturated with water vapor at room temperature by passing it through water which had been previously weighed. The gaseous mixture was then passed through a quartz tube and over a platinum boat containing the  $B_2O_3$  at a controlled temperature. The transpired gas was collected over water. The  $B_2O_3$  had been preheated to constant weight at  $1200^\circ K$  and a pressure of one micron. The platinum boat was placed inside a quartz boat so that any  $B_2O_3$  overflowing it would not come in contact with the quartz tube. The furnace temperature was controlled automatically within a range of  $\pm 10^\circ$  in each of the experimental runs. The length of time for the experimental runs varied between 6 and 72 hours.

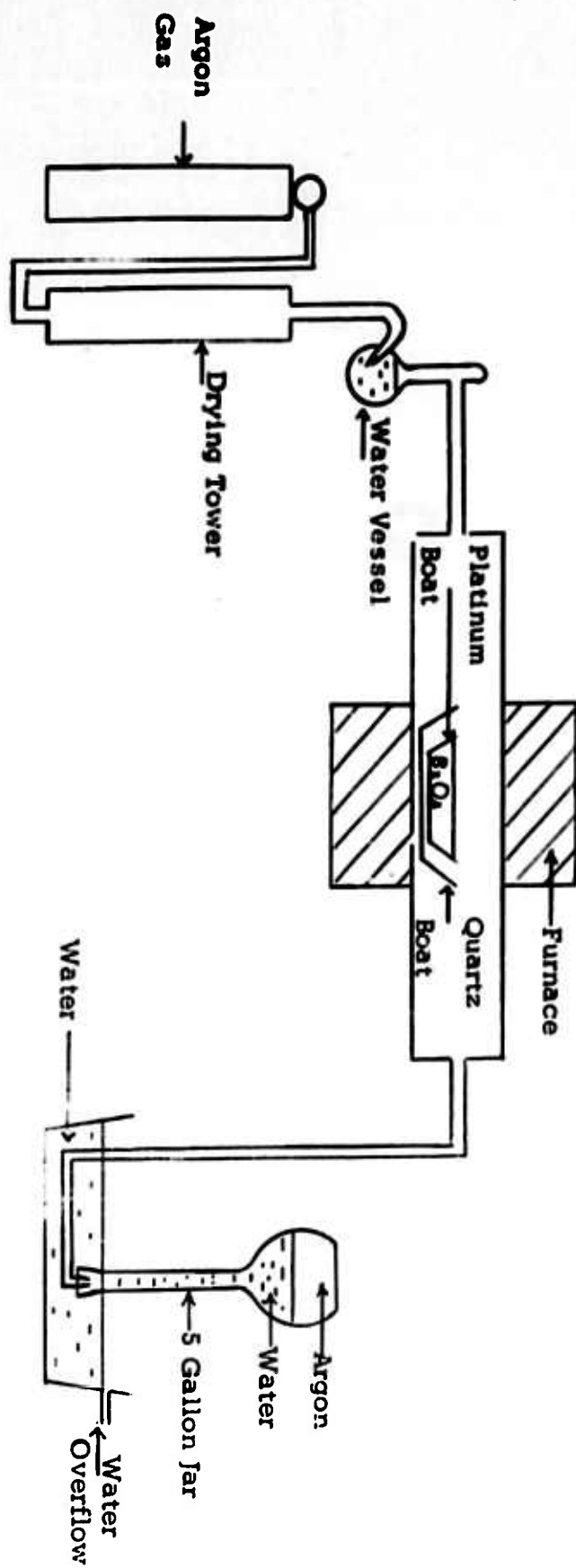
The correct flow rate of the gaseous phase over the solid or liquid phase is of utmost importance in transpiration theory.<sup>10</sup> In order to ascertain the proper flow rate for the establishment of equilibrium, numerous experimental determinations of  $K_3$  were made as a function of the flow rate. A plot of  $K_3$  versus the flow rate is shown in Fig. 5. The figure shows the equilibrium zone to be between 2.0 and 3.0 cc per minute at a temperature of  $1316^\circ K$ . Although numerous data have been taken to date, only those data taken at flow rates of between 2.0 and 3.0 cc per minute are reported in the following section.

The results of the preliminary experiments having the proper flow rates are listed in Table V. The free energies listed in Table V were obtained from the classical thermodynamic relationship

$$\Delta F = - RT \ln K_3$$

The partial pressure ratios listed in columns 8 and 9 were evaluated by means of equations (37), (38) and (50). Since the optimum flow rate has been determined at only one temperature, i.e. at  $1316^\circ K$ , a least squares analysis of the data for the entropy and enthalpy changes of the reaction will be deferred until more data are available.





**Fig. 4. Schematic Drawing of Transpiration Apparatus**

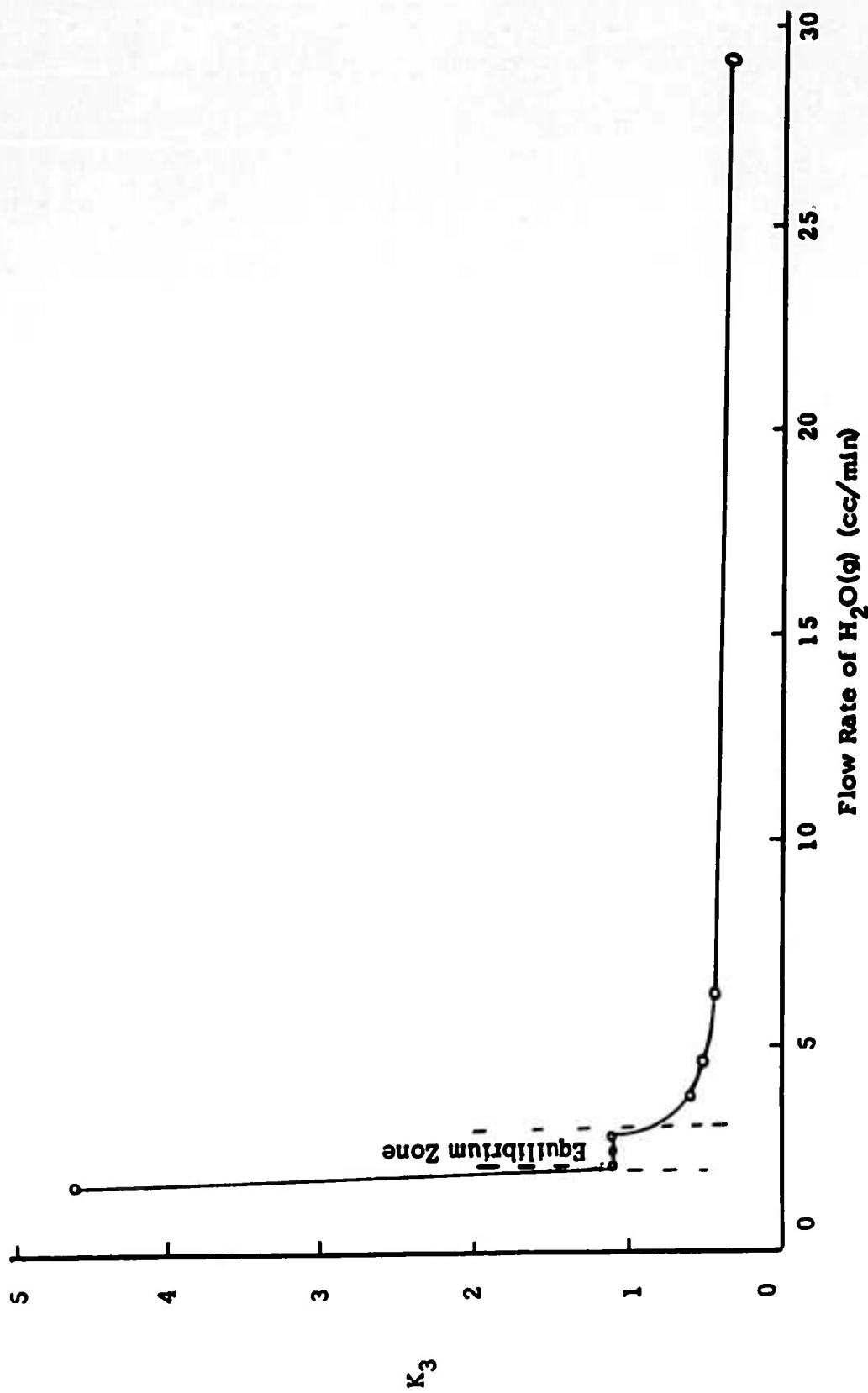


Fig. 5.  $K_3$  as a function of Flow Rate at  $1316^\circ K$

TABLE V  
EXPERIMENTAL TRANSPIRATION DATA AND CALCULATED FREE ENERGIES  
FOR THE REACTION  
 $3/2\text{B}_2\text{O}_3(l) + 3/2\text{H}_2\text{O}(g) \rightleftharpoons (\text{HBO}_2)_3$

T (°K)	Flow Rate (cc/min)	Weight Loss of $\text{B}_2\text{O}_3$ (moles)	Weight Loss of $\text{H}_2\text{O}$ (moles)	Moles of Argon Transpired	K <sub>3</sub>	$\Delta F$ (kcal/mole)	Calculated Ratios	
							$\frac{P_{\text{HBO}_2}}{P_{(\text{HBO}_2)_3}}$	$\frac{P_{\text{H}_3\text{BO}_3}}{P_{(\text{HBO}_2)_3}}$
1137	3.0	0.000402	0.0130	0.504	0.127	4.66	0.088	0.037
1204	2.0	0.000224	0.00230	0.106	0.431	2.01	0.086	0.010
1281	2.1	0.000570	0.00264	0.112	0.912	0.23	0.087	0.003
1281	2.1	0.000663	0.00274	0.117	1.02	-0.05	0.101	0.004
1349	2.0	0.000961	0.00125	0.077	3.97	-3.70	0.084	0.001
1423	2.1	0.000551	0.000342	0.030	9.82	-6.47	0.102	0.000
1316	2.6	0.000834	0.00327	0.148	1.10	-0.25	0.150	0.004
1316	2.1	0.000231	0.00835	0.035	1.16	-0.39	0.132	0.003
1316	2.2	0.000253	0.000896	0.039	1.20	-0.48	0.133	0.003

**D. Future Work**

During the next period we plan to determine the equilibrium constant for reaction (29) at ten or more different temperatures after having determined the optimum flow rate at each temperature.

## REFERENCES

1. Farber, M. et al, "Thermodynamics of Reactions Involving Light Metal Oxides and Propellant Gases," Rocket Power, Inc., Fourth Quarterly Report, QR-1987-4, ARPA, February - May 1961.
2. JANAF Interim Thermochemical Tables, The Dow Chemical Company, Midland, Michigan, Volumes 1 and 2, December 31, 1960.
3. Petersen, H. et al, "Thermodynamics of Reactions Involving Light Metal Oxides and Propellant Gases," Rocket Power, Inc., Fifth Quarterly Report, QR-1987-5, May - August 1961.
4. Brewer, L. and Searcy, A., JACS 73, 5308 (1951).
5. Dushman, S., "Vacuum Technique," John Wiley and Sons, New York, p. 90-99.
6. Farber, M. et al, "Thermodynamics of Reactions Involving Light Metal Oxides and Propellant Gases," Rocket Power, Inc., Third Quarterly Report, QR-1987-3, ARPA, November 1960 - February 1961.
7. Fisher, H., Lehmann, W., and Shapiro, I., J. Phys. Chem., 65, 1166 (1961).
8. Hildenbrand, D., "An Experimental Program for Obtaining the Thermodynamic Properties of Propellant Combustion Products," Aeronutronic Division of Ford Motor Co., First Quarterly Report, Publication No. U-1376, 15 September 1961.
9. Meschi, D.J., Chupka, W. A., and Berkowitz, J., "Heterogeneous Reaction Studies by Mass Spectrometry. I. Reactions of  $B_2O_3(s)$  with  $H_2O(g)$ ," J. Chem. Phys., 33, 530 (1960).
10. Farber, M. et al, "Thermodynamics of Reactions Involving Light Metal Oxides and Propellant Gases," Rocket Power, Inc., Second Quarterly Report, QR-1987-2, ARPA, August - November 1960.

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